

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		CM2100 U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/937262
INTERNATIONAL APPLICATION NO. PCT/US00/10072 10272	INTERNATIONAL FILING DATE 13 April 2000	PRIORITY DATE CLAIMED 30 April 1999
TITLE OF INVENTION Cleaning Compositions and Tablets		
APPLICANT(S) FOR DO/EO/US HEINZMAN, Stephen Wayne et al.		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.		
<ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l). <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input checked="" type="checkbox"/> A copy of the International Application was filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> has been transmitted by the International Bureau. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> have been transmitted by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input checked="" type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). <p>Items 11. to 16. below concern document(s) or information included:</p> <ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input checked="" type="checkbox"/> A change of power of attorney and/or address letter. <input type="checkbox"/> Other items or information: <p><i>EL 483621006715</i></p> <p>*Express Mail® mailing label number Date of Deposit <i>24 Sep 2001</i></p> <p>I hereby certify that this paper/fees is being deposited with the United States Postal Service, Express Mail Post Office addressee, in accordance with 37 CFR 1.10, on the date indicated above and is addressed to The Assistant Commissioner of Patents, Washington, D.C. 20231</p> <p>Administrator Mailing Application Signature <i>Douglas C. Byrd</i></p>		

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
09/937262		PCT/US00/10272		CM2100	
				CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT = \$710					
Surcharge of \$130.00 for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(c)).					
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	14-20 =	0	x \$18.00	\$0	
Independent Claims	3 -3 =	0	x \$80.00	\$0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				\$270.00	
TOTAL OF ABOVE CALCULATIONS = \$710					
Processing fee of \$130.00 for furnishing the English translation later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(l)).					
TOTAL NATIONAL FEE = \$710					
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). \$40.00 per property +					
TOTAL FEES ENCLOSED = \$710					
				Amount to be refunded	\$
				charged	\$
<p>a. [] A check in the amount of \$ ____ to cover the above fees is enclosed.</p> <p>b. [x] Please charge my Deposit Account No. <u>16-2480</u> in the amount of \$ <u>710</u> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. [x] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>16-2480</u>. A duplicate copy of this sheet is enclosed.</p>					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
M. Dressman, Patent Attorney Customer Number 27752				 Signature <u>T. David Reed</u> Name <u>32,931</u> Registration Number	

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Case CM-2100

In the Matter of :
US National Phase Entry :
Under 35 USC 371 from :
International Application of :
Heinzman et al., :
Int'l Application No. PCT/US00/10272 : Group Art Unit : N/A
Filed on April 13, 2000 : Examiner : N/A
:

For Cleaning Compositions And Tablets :

PRELIMINARY AMENDMENT

The Assistant Commissioner of Patents

Washington, D.C. 20231

Dear Sir:

Before computing the fees for entering the captioned International Application into the US National Phase, please enter the following amendments.

IN THE CLAIMS:

Please delete current claims 1-15 and replace with the new claims 16-29 below.

16. A cleaning composition or component thereof comprising a compressed clay component.
17. A tablet comprising an active ingredient and a compressed clay component.
18. A tablet, composition or component according to claim 16 obtainable by compressing a clay material to form a compressed clay component and subsequently incorporation of the compressed clay component in the tablet, cleaning composition or component.
19. A tablet, composition or component according to claim 16, wherein the clay component is obtained by compression of a clay material with a pressure of at least 10 MPa.

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20. A tablet, composition or component according to claim 19 wherein the compressed clay component is in the form of particles whereof at least 90% by weight has a particle size of from 200 microns to 1500 microns.
21. A tablet, composition or component according to claim 16 whereby the clay component comprises a binder material.
22. A tablet, composition or component according to any of claim 16 whereby the clay component is free of any added binder materials other than water.
23. A tablet, composition or component according to claim 16 whereby the clay comprises a smectite clay.
24. A tablet, composition or component according to claim 16 comprising one or more additional disintegrating agents, preferably a water soluble salt such as sodium acetate, and/or a microcrystalline cellulose.
25. A tablet or composition according to claim 16 being a solid laundry or dishwashing tablet or composition and comprising from 0.5% to 30% by weight of the composition or tablet of the compressed clay component.
26. A tablet according to claim 17 being a pharmaceutical tablet.
27. A compressed clay granule according to claim 16 comprising a clay material and an effervescence system which comprises an acid source and a carbonate source, and/or a disintegrating agent, selected from the group consisting of water-swellable materials, microcrystalline cellulose, water soluble salts and mixtures thereof.
28. A pharmaceutical composition, plant nutrient composition or plant fertilizer composition comprising a compressed clay component.
29. A method of providing softening of fabrics by contacting said fabrics with a cleaning composition or tablet according to claim 23.

Conclusion

Support for these amendments is found in the claims as originally filed. These amendments are entered to bring the claims into conformance with 37 CFR §1.75; no new matter is added.

Respectfully submitted,

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Cincinnati, Ohio
K/Dressman/PrelAmend/PACM2100

Cleaning Compositions and Tablets

Technical Field

The present invention relates to various uses for compressed clay material and in particular to tablets or cleaning compositions comprising compressed clay.

Background to the Invention

Clays have been used for several years in detergents to provide softening of the fabrics washed with the compositions. They have been described as materials which can be dry-added to the other detergent granules, or can be mixed with other ingredients. EP-A-313146 described agglomerates containing 60% to 99% clay, wax and a humectant, which are added to a detergent composition.

Clay has also been mentioned to aid breaking up of tablets, which is for example described in EP-A-328880 and EP-A-799886.

The inventors have now found that when a clay material is compressed prior to incorporation into a tablet or in a cleaning composition, improved disintegration, dispensing and/or dissolution is achieved. They found for example that tablets comprising clay which is compressed prior to incorporation into a tablet, disintegrate more rapidly than tablets comprising the same clay material which has not been compressed prior to incorporation into a tablet. They also found that in particular the amount of pressure used for the compression of the clay is of importance to obtain clay particles which aid disintegration, dispensing or dissolution.

The inventors also found that in cleaning compositions the compressed clay component improves the dispensing and/or dissolution of the detergent ingredients. This is believed to be due to the disintegration initiated by the compressed clay, of product lumps formed

by caking or gelling of the product, in particular upon contact with water or moisture, such as in the dispensing drawer of a washing machine.

The inventors also found that when softening clays are compressed and than incorporated in cleaning compositions or tablets, not only improved disintegration, dispensing or dissolution is obtained, but also good softening of the fabrics. They found that even improved softening can be achieved compared to clay agglomerates comprising binder materials such as wax.

Summary of the invention

The present invention provides cleaning composition or component thereof comprising a compressed clay component.

The invention also relates to tablets, preferably cleaning tablets, pharmaceutical tablets, plant nutrient tablets, plant fertilizer tablets, comprising an active ingredient and a compressed clay component.

Also provided are tablets, compositions or components whereby the clay component is obtained by compression of a clay material with a pressure of at least 10 MPa.

The tablets, compositions or components are for example obtainable by compressing a clay material to form a compressed clay component and subsequently incorporation of the compressed clay component in the tablet, cleaning or detergent composition or component.

The tablets or compositions are preferably solid cleaning compositions or tablets, preferably laundry compositions or tablets.

The invention also relates to the use of a compacted clay component in a granular composition or tablet, in particular a cleaning composition or tablet plant nutrient

composition or tablet, plant fertilizer compositions or tablet, or pharmaceutical compositions or tablet, to improve the dissolution or disintegration of the composition or tablet.

Detailed description of the invention

Compressed clay component.

The compressed clay component herein can comprise any clay material known in the art, however preferably it comprises a clay material which can aid disintegration or dissolution or dispensing to some extent, without being compressed. When used in cleaning compositions or tablets herein, the clay material of the compressed clay component is preferably a clay material which provides softening of fabrics.

It should be understood for the purpose of the invention that the compressed clay component is compressed prior to incorporation in the compositions, components or tablets herein. However, the clay material of the compressed clay component may be mixed with other ingredients prior to compression, as described in more detail hereinafter.

The compressed clay component can be obtained by any method comprising the step of submitting a clay material, optionally mixed with other ingredients, to a pressure. For the purpose of the invention, agglomeration of clay without any intentional, application of pressure, as known in the art for example from EP-A-313146, is not to be understood as a method of applying pressure on a clay material.

A preferred process comprises the steps of submitting the clay material to a pressure of at least 10MPa, or even at least 20MPa or even at least 40MPa. This can for example be done by tabletting or roller compaction of a clay material, optionally together with one or more other ingredients, to form a clay tablet or sheet, preferably followed by size reduction, such as grinding, of the compressed clay sheet or tablet, to form compressed clay particles. The particles can then be incorporated in a tablet or cleaning composition.

Tabletting methods and roller compaction methods are known in the art. For example, the compression of the clay can be done in a Lloyd 50K tablet press or with a Chilsonator roller compaction equipment, available from Fitzpatrick Company.

Various size reduction methods or grinding methods are also commonly known in the art. The size reduction step may comprise two or more individual size reduction or grinding phases, for example first breaking up the tablet or sheet into smaller lumps, and then grinding the lumps to form granules

The clay component is thus preferably in the form of granules. Preferably, at least 90% by weight of the particulate clay component has a particle size of from 150 microns to 2000 microns, more preferably from 200 microns to 1500 microns or even from 250 microns to 1200 microns. More preferably 90% of the particles has a particle size of from 400 microns to 1100 microns or even from 500 microns to 1000 microns. It may be preferred that substantially no fine particles of a particle size below 100 microns or even below 150 microns are present.

Particles of the required particle size can for example be obtained by sieving the particles obtained by the size reduction or grinding step(s), by using sieves of the applicable particle size and collecting the fraction which remains on the sieve corresponding to the minimum particle size and which passes the sieve corresponding to the maximum particle size.

The clay component may comprise additional ingredients, for example a binder material. Binder materials which can be used are those commonly used in tablets, as described herein after. Preferred binder materials for the clay component herein include liquids such as water, but also viscous or solid materials which can be melted at a temperatures whereby the clay is not affected. Preferred binders are oils, waxes, glycerol, polyalkylene glycols, (nonionic) surfactants and/or water.

Granulation aids, desiccants and/ or humectants may also be present.

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The clay component preferably comprises at least 40% or even at least 60% by weight of a clay material, including the water of hydration comprised in the clay material.

Preferably, the clay component comprises at least 70% or even at least 80% or even at least 90% or even at least 95% by weight of the clay material. It may be preferred that the clay component consist of clay and water and minor ingredients which occur naturally in the clay.

Highly preferred are smectite clays, as for example are disclosed in the US Patents No.s 3,862,058 3,948,790, 3,954,632 and 4,062,647 and European Patents No.s EP-A-299,575 and EP-A-313,146 all in the name of the Procter and Gamble Company.

The term smectite clays herein includes both the clays in which aluminium oxide is present in a silicate lattice and the clays in which magnesium oxide is present in a silicate lattice. Typical smectite clay compounds include the compounds having the general formula $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$ and the compounds having the general formula $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Smectite clays tend to adopt an expandable three layer structure.

Specific examples of suitable smectite clays include those selected from the classes of the montmorillonites, hectorites, volchonskoites, nontronites, saponites and sauconites, particularly those having an alkali or alkaline earth metal ion within the crystal lattice structure.

Preferred may be three-layer, expandable alumino-silicates which are characterised by a dioctahedral crystal lattice, while the expandable three-layer magnesium silicates have a trioctahedral crystal lattice.

As noted herein above, the clays employed in the compositions of the instant invention contain cationic counterions such as protons, sodium ions, potassium ions, calcium ion, magnesium ion, and the like. It is customary to distinguish between clays on the basis of

one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation:

$$\text{smectite clay (Na)} + \text{NH}_4\text{OH} \rightarrow \text{smectite clay (NH}_4\text{)} + \text{NaOH}$$

Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq./100 g.). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which, in turn, is determined at least in part by the lattice structure, and the like.

Smectites, such as nontonite, having an ion exchange capacity of around 70 meq/100 g., and montmorillonite, which has an ion exchange capacity greater than 70 meq/100 g., have been found to be useful herein, in that they are effectively deposited on the fabrics to provide the desired softening benefits. Accordingly, preferred clay materials useful herein can be characterised as expandable, three-layer smectite-type clays having an ion exchange capacity of at least about 50 meq/100 g.

The preferred clays herein are available under various tradenames, for example, Thixogel #1 and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC and Volclay #325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R.T. Vanderbilt. It is to be recognised that such smectite-type minerals obtained under the foregoing tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

Montmorillonite clays are preferred herein, and sodium or calcium montmorillonite are particularly preferred to provide softening. Suitable smectite clays, particularly

montmorillonites, are sold by various suppliers including English China Clays, Laviosa, Georgia Kaolin and Colin Stewart Minchem. Gelwhite GP is an extremely white form of smectite clay and is therefore preferred when formulating white compositions or tablets herein. Volclay BC, which is a smectite-type clay mineral containing at least 3% of iron (expressed as Fe₂O₃) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use herein and is preferred from the standpoint of product performance.

Organophilic clays may also be used herein. These are hydrophobically modified clays which have organic ions replacing inorganic metal ions by ion exchange processes known in the art. These kinds of clay are readily mixable with organic solvent and have the capability to absorb organic solvent at the interlayers. Suitable examples of organophilic clays useful in the invention are Bentone SD-1, SD-2 and SD-3 from Rheox of Hightstown, N.J.

The particle size of the clay materials used to form the compressed clay component herein will depend on the final particle size of the clay component. Preferably, the clay material prior to compression has a particle size of from 0.01 μm to 800 μm, more preferably from 1 μm to 400 μm, most preferably from 5 μm to 200 μm or even to 150 μm.

It may be highly preferred that the compressed clay components, tablets, components or compositions herein comprise also one or more additional disintegrating agents or dispensing agents or wicking agents, in addition to the compressed clay component.

Preferred disintegrating agents herein are those which will swell upon contact with water and break the tablet or granule comprising the disintegrating agent in small pieces. This will improve the dispersion or dispensing of the product in the solution. Possible disintegrants are described in Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch: natural, modified or pregelatinized starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin

gum, tragacanth gum; croscarmylose sodium, crospovidone, cellulose, carboxymethyl cellulose, algenic acid and its salts including sodium alginate, silicone dioxide, polyvinylpyrrolidone, soy polysacharides, ion exchange resins and mixtures thereof.

Highly preferred additional disintegrating agents for the granular detergent compositions of the invention but in particular for the tablets of the invention, are preferably water-swellable celluloses such as Solka-floc and Arbocel, and microcrystalline cellulose such as Lattice, available from FMC, and water soluble salts such as sodium acetate.

Non compressed clays may also be present as additional ingredient of the tablets or cleaning compositions herein, in particular when the tablets or compositions are used for fabric softening.

Also preferred may be in the compressed clay components, tablets or compositions of the invention, to incorporate an effervescence system, capable of providing a gas upon contact with water. Preferably such a system comprises an acid source and a carbonate source, capable of reacting together in the presence of water to form carbon dioxide gas.

Suitable acids to be used herein include solid organic, mineral or inorganic acids, salts or derivatives thereof or a mixture thereof. It may be preferred that the acids are mono-, bi- or tri-protonic acids. Such acids include mono- or polycarboxylic acids preferably citric acid, adipic acid, glutaric acid, 3 chetoglutaric acid, citramalic acid, tartaric acid, maleic acid, fumaric acid, malic acid, succinic acid, malonic acid. Such acids are preferably used in their acidic forms, and it may be preferred that their anhydrous forms are used, or mixtures thereof. Derivatives also include ester of the acids. Surprisingly, it has now been found that by using tartaric, maleic and in particular malic acid as the acid in the dry effervescent granules, said granules deliver improved physical and/or chemical stability upon prolonged storage periods.

Suitable carbonate sources include carbonate, bicarbonate and percarbonate salts, in particular bicarbonate and/or carbonate. Suitable carbonates to be used herein include

carbonate and hydrogen carbonate of potassium, lithium, sodium, and the like amongst which sodium and potassium carbonate are preferred. Suitable bicarbonates to be used herein include any alkali metal salt of bicarbonate like lithium, sodium, potassium and the like, amongst which sodium and potassium bicarbonate are preferred. Bicarbonate may be preferred to carbonate, because it is more weigh effective, i.e., at parity weigh bicarbonate is a larger C0₂ "reservoir" than carbonate. However, the choice of carbonate or bicarbonate or mixtures thereof in the dry effervescent granules may be made depending on the pH desired in the aqueous medium wherein the dry effervescent granules are dissolved. For example where a relative high pH is desired in the aqueous medium (e.g., above pH 9.5) it may be preferred to use carbonate alone or to use a combination of carbonate and bicarbonate wherein the level of carbonate is higher than the level of bicarbonate, typically in a weight ratio of carbonate to bicarbonate from 0.1 to 10, more preferably from 1 to 5 and most preferably from 1 to 2.

The cleaning compositions, component or tablets may preferably contain a clay flocculating agent, preferably present at a level of from 0.005% to 10%, more preferably from 0.05% to 5%, most preferably from 0.1% to 2% by weight of the composition.

The clay flocculating agent functions such as to bring together the particles of clay compound in the wash solution and hence to aid their deposition onto the surface of the fabrics in the wash. This functional requirement is hence different from that of clay dispersant compounds which are commonly added to laundry detergent compositions to aid the removal of clay soils from fabrics and enable their dispersion within the wash solution.

Preferred as clay flocculating agents herein are organic polymeric materials having an average weight of from 100,000 to 10,000,000, preferably from 150,000 to 5,000,000, more preferably from 200,000 to 2,000,000.

Suitable organic polymeric materials comprise homopolymers or copolymers containing monomeric units selected from alkylene oxide, particularly ethylene oxide, acrylamide,

acrylic acid, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Homopolymers of, on particular, ethylene oxide, but also acrylamide and acrylic acid are preferred.

European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe preferred organic polymeric clay flocculating agents for use herein.

Inorganic clay flocculating agents are also suitable herein, typical examples of which include lime and alum.

The flocculating agent is preferably present in a detergent base granule such as a detergent agglomerate, extrudate or spray-dried particle, comprising generally one or more surfactants and builders.

It may be preferred that clay material used to prepare the compressed clay component herein has a free moisture content of less than 30%, preferably less than 23% or even less than 18% or even less than 12%, which means that its free moisture content is such that when the 10 gram of the clay material is oven-dried at 105°C for 1 hour under a draught, the clay material looses less than 30% of its original weight, preferably less than 23% or even less than 18% or even less than 12%.

Tablets

The tablets herein can be any tablet used to deliver an active ingredient to a medium comprising a solvent. Preferred tablets forms are pharmaceutical tablets, to deliver active ingredients such as medicaments to a aqueous medium, tablets comprising plant nutrients or fertilisers or tablets comprising pesticides.

Highly preferred are detergent tablets, delivering detergent actives to the cleaning solution, such as preferably laundry or dish washing solutions or hard-surface cleaning solution. Preferred ingredients of cleaning tablets herein are described hereinafter.

It may be preferred that the tablet are laundry tablets which provide softening of fabrics in the wash.

When the tablets are cleaning or detergent tablets, they preferably comprise the compressed clay component at a level of from 0.05% to 30% by weight of the tablet, more preferably from 1% to 20% or even from 2% to 15% or even 3% to 12% by weight.

The tablet may comprise a coating. The tablet may be coated so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is preferably also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dispersed under alkaline conditions, or is readily emulsified by surfactants. This contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also avoids deposition of particles or lumps of coating material on the laundry load.

It may be preferred that the coating comprises one or more disintegrating agent as described herein, or even a compressed clay component herein.

Suitable coating materials are carboxylic acids, preferably dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof. The coating material preferably has a melting point of from 40°C to 200°C.

The coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material.

In a), the coating material is applied at a temperature above its melting point, and solidifies on the tablet. In b), the coating is applied as a solution, the solvent being dried

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to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. Clearly substantially insoluble materials having a melting point below 40°C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 200°C are not practicable to use. Preferably, the materials melt in the range from 60°C to 160°C, more preferably from 70°C to 120°C.

By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

It may be preferred that the tablets herein comprise one or more binders. For example, non gelling binders can be integrated to the particles forming the tablet in order to further facilitate dispersion.

If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e. ethoxylated hexamethylene diamine quaternary compounds, bishexamethylene triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

Non-gelling binder materials are preferably used in an amount within the range from 0.1 to 15% of the composition, more preferably below 5% and especially if it is a non laundry active material below 2% by weight of the tablet.

It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials, and not as liquids.

Tablet Manufacture

Detergent or cleaning tablets herein can be prepared simply by mixing the solid ingredients, including the compressed clay, together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.

The ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 20000N and most preferably of less than 10000 N. However, when coating agents are used to coat the tablet core, even lower forces can be used to make the core of the tablet, such as for example below 5000N or even below 3000N.

The particulate material, not being the compressed clay component, used for making the tablet of this invention can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige(R) CB and/or Lodige(R) KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sintering, etc. Individual particles can also be any other particle, granule, sphere or grain. The components of the particulate material may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components of the particulate material. Other liquid ingredients may also be sprayed on to the mix of components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

As described above for the compressed clay component, the tablets containing the compressed clay component, such as detergent tablets, may be manufactured by using any compacting process, such as tabletting, briquetting, or extrusion, preferably tabletting. Suitable equipment, which can also be used to make the compressed clay component herein, includes a standard single stroke or a rotary press (such as Courtoy(R), Korch(R), Manesty(R), or Bonals(R)). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter

(or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m², preferably not exceed 30000 kN/m², more preferably not exceed 5000 kN/m², even more preferably not exceed 3000kN/m² and most preferably not exceed 1000kN/m². In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least 1.0 g/cc, and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25 g/cc and most preferably of less than 1.1 g/cc.

Multi-layer tablets can be made by known techniques.

Cleaning compositions and components

The compressed clay component can be used in any composition or component thereof, to improve the dissolution or disintegration thereof, in particular in cleaning compositions, pharmaceutical compositions, plant nutrient compositions or plant fertilizer compositions, provided that these compositions allow incorporation of a granular clay component. Thus, generally the compositions will be solid compositions, in particular granular compositions.

Highly preferred compositions are cleaning compositions or component thereof.

The compositions can take a variety of physical forms including granular, flake, pastille and bar and even liquid forms. Liquids may be aqueous or non-aqueous and may be in the form of a gel. The compositions may be pre-treatment compositions or may be conventional washing detergents. The compositions are particularly granular detergent compositions, preferably the so-called concentrated compositions adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

Such granular detergent compositions or components thereof can be made via a variety of methods, including spray-drying, dry-mixing, extrusion, agglomerating and granulation..

Cleaning compositions or components herein, and also the cleaning tablets described above, preferably comprise the clay at a level of from 0.05% to 30% by weight of the tablet, more preferably from 1% to 20% or even from 2% to 15% or even 3% to 12% by weight.

The compressed clay component may be comprised in a detergent granule. However, it may be preferred that the compressed clay is present as a separate granular component of the composition, to aid dissolution, dispersion or dispensing of the composition, in particular in the event that caking or gelling occurs upon contact with water. This may in particular occur when the compositions comprise gelling ingredients such as nonionic surfactants. The incorporation of the compressed clay component as separate granule may in particularly be preferred when the compressed clay component has the preferred larger particle sizes, 90% by weight being from 400 to 1100 microns or even from 500 to 1000 microns.

When the compressed clay component is incorporated in a detergent granule, it is clear that the detergent granule will be of a larger particle size than the clay component. The clay component may be particularly useful in compositions comprising detergent granules of a mean particle size of above 350 microns, preferably above 400 or even 500 microns or even above 600 or even 700 microns.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of sieves, preferably Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

In a preferred embodiment, the composition preferably comprises whereof (not including the compressed clay granules when present as separate granular components) at least 60%, more preferably at least 80% by weight have an average particle size, by weight, of from 450 microns to 1400 microns, preferably from 500 or even 600 microns to 1100

microns or even 700 to 1000 microns. It may even be preferred that the compositions comprises less than 20% or even less than 10% or even less than 5% by weight of particulate components (not including the compressed clay granules when present as separate granular components) of a particle size of less than 200 microns, or even less than 350 microns or even less than 425 microns; it may also be preferred the composition comprise less than 20% or even less than 10% or even less than 5% by weight of the composition, of particulate components (not including the compressed clay granules when present as separate granular components) of a particle size of more than 1700 microns, or even more than 1400 microns or even more than 1180 microns.

The detergent compositions or component thereof may also comprise additional disintegrating agents and/ or effervescence sources.

Additional ingredients of cleaning compositions and tablets

The compositions and detergent tablets in accord with the invention contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition or component, and the precise nature of the washing operation for which it is to be used.

The compositions of the invention preferably contain one or more additional detergent components selected from surfactants, bleaches, bleach catalysts, alkalinity systems, builders, phosphate-containing builders, organic polymeric compounds, enzymes, suds suppressors, lime soap, dispersants, soil suspension and anti-redeposition agents soil releasing agents, perfumes, brightners, photobleaching agents and additional corrosion inhibitors.

Surfactant

The compositions in accord with the invention preferably contain one or more surfactants selected from anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic Surfactant

The compositions in accord with the present invention preferably comprise an additional anionic surfactant. Essentially any anionic surfactants useful for detergative purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate and sulfonate surfactants are preferred.

Highly preferred are surfactants systems comprising a sulfonate and a sulfate surfactant, preferably a linear or branched alkyl benzene sulfonate and alkyl ethoxysulfates, as described herein, preferably combined with a cationic surfactants as described herein.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters), diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic Sulfate Surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₁₀-C₁₈ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and/or sulfonate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic Sulfonate Surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic Carboxylate Surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{C}(\text{OOH})\text{M}^+$ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $\text{RO}-(\text{CHR}_1-\text{CHR}_2-\text{O})-\text{R}_3$ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R₃ is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Certain soaps may also be included as suds suppressors.

Alkali Metal Sarcosinate Surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON(R¹)CH₂COOM, wherein R is a C₅-C₁₇ linear or branched alkyl or alkenyl group, R¹ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Alkoxylated Nonionic Surfactant

Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic Alkoxylated Alcohol Surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic Polyhydroxy Fatty Acid Amide Surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein : R₁ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R₂ is a C₅-C₃₁ hydrocarbyl, preferably straight-chain C₅-C₁₉ alkyl or alkenyl, more preferably straight-chain C₉-C₁₇ alkyl or alkenyl, most preferably straight-chain C₁₁-C₁₇ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycetyl.

Nonionic Fatty Acid Amide Surfactant

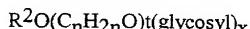
Suitable fatty acid amide surfactants include those having the formula: $R^6CON(R^7)_2$ wherein R⁶ is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon

atoms and each R⁷ is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and -(C₂H₄O)_xH, where x is in the range of from 1 to 3.

Nonionic Alkylpolysaccharide Surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula:



wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Amphoteric Surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula R³(OR⁴)_xN⁰(R⁵)₂ wherein R³ is selected from an alkyl, hydroxyalkyl, acylamidopropyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R⁴ is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C₁₀-C₁₈ alkyl dimethylamine oxide, and C₁₀-C₁₈ acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic Surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions in accord with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, each R¹ is typically C₁-C₃ alkyl, and R² is a C₁-C₅ hydrocarbyl group. Preferred betaines are C₁₂₋₁₈ dimethyl-ammonio hexanoate and the C₁₀₋₁₈ acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Cationic Surfactants

Suitable cationic surfactants to be used in the detergent herein include the quaternary ammonium surfactants. Preferably the quaternary ammonium surfactant is a mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Preferred are also the mono-alkoxylated and bis-alkoxylated amine surfactants.

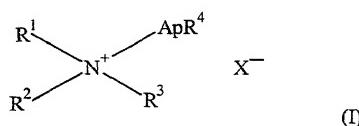
Another suitable group of cationic surfactants which can be used in the detergent compositions or components thereof herein are cationic ester surfactants. The cationic ester surfactant is a, preferably water dispersible, compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group.

Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

In one preferred aspect the ester linkage and cationically charged group are separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), preferably from three to eight atoms, more preferably from three to five atoms, most preferably three atoms. The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain. Thus spacer groups having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example -CH₂-O- CH₂- and -CH₂-NH-CH₂- linkages are included. In a preferred aspect the spacer group chain comprises only carbon atoms, most preferably the chain is a hydrocarbyl chain.

Cationic mono-alkoxylated amine surfactants

Highly preferred herein are cationic mono-alkoxylated amine surfactant preferably of the general formula I:

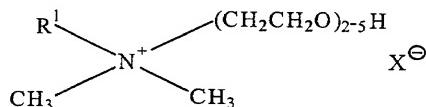


wherein R¹ is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about 6 to about 14 carbon atoms; R² and R³ are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl, most preferably both R² and R³ are methyl groups; R⁴ is selected from hydrogen (preferred), methyl and ethyl; X⁻ is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A

is a alkoxy group, especially a ethoxy, propoxy or butoxy group; and p is from 0 to about 30, preferably 2 to about 15, most preferably 2 to about 8.

Preferably the ApR⁴ group in formula I has p=1 and is a hydroxyalkyl group, having no greater than 6 carbon atoms whereby the —OH group is separated from the quaternary ammonium nitrogen atom by no more than 3 carbon atoms. Particularly preferred ApR⁴ groups are —CH₂CH₂OH, —CH₂CH₂CH₂OH, —CH₂CH(CH₃)OH and —CH(CH₃)CH₂OH, with —CH₂CH₂OH being particularly preferred. Preferred R¹ groups are linear alkyl groups. Linear R¹ groups having from 8 to 14 carbon atoms are preferred.

Another highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula



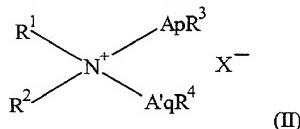
wherein R¹ is C₁₀-C₁₈ hydrocarbyl and mixtures thereof, especially C₁₀-C₁₄ alkyl, preferably C₁₀ and C₁₂ alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

As noted, compounds of the foregoing type include those wherein the ethoxy (CH₂CH₂O) units (EO) are replaced by butoxy, isopropoxy [CH(CH₃)CH₂O] and [CH₂CH(CH₃O)] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

The levels of the cationic mono-alkoxylated amine surfactants used in detergent compositions of the invention is preferably from 0.1% to 20%, more preferably from 0.2% to 7%, most preferably from 0.3% to 3.0% by weight of the composition.

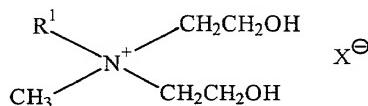
Cationic bis-alkoxylated amine surfactant

The cationic bis-alkoxylated amine surfactant preferably has the general formula II:



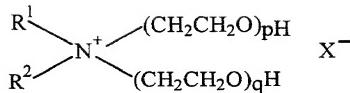
wherein R¹ is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R² is an alkyl group containing from one to three carbon atoms, preferably methyl; R³ and R⁴ can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X⁻ is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C₁-C₄ alkoxy, especially ethoxy, (i.e., -CH₂CH₂O-), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both n and q are 1.

Highly preferred cationic bis-alkoxylated amine surfactants for use herein are of the formula



wherein R¹ is C₁₀-C₁₈ hydrocarbyl and mixtures thereof, preferably C₁₀, C₁₂, C₁₄ alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in a preferred compound R¹ is derived from (coconut) C₁₂-C₁₄ alkyl fraction fatty acids, R² is methyl and A¹R³ and A¹'R⁴ are each monoethoxy.

Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:



wherein R¹ is C₁₀-C₁₈ hydrocarbyl, preferably C₁₀-C₁₄ alkyl, independently p is 1 to about 3 and q is 1 to about 3, R² is C₁-C₃ alkyl, preferably methyl, and X is an anion, especially chloride or bromide.

Other compounds of the foregoing type include those wherein the ethoxy (CH₂CH₂O) units (EO) are replaced by butoxy (Bu) isopropoxy [CH(CH₃)CH₂O] and [CH₂CH(CH₃O] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

Perhydrate Bleaches

An preferred additional components of the compositions is a perhydrate bleach, such as metal perborates, metal percarbonates, particularly the sodium salts. Perborate can be mono or tetra hydrated. Sodium percarbonate has the formula corresponding to 2Na₂CO₃.3H₂O₂, and is available commercially as a crystalline solid.

Potassium peroxyomonopersulfate, sodium per is another optional inorganic perhydrate salt of use in the detergent compositions herein.

Organic Peroxyacid Bleaching System

A preferred feature of the composition is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches, such as the perborate bleach of the claimed invention. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition.

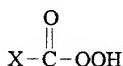
Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Peroxyacid Bleach Precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



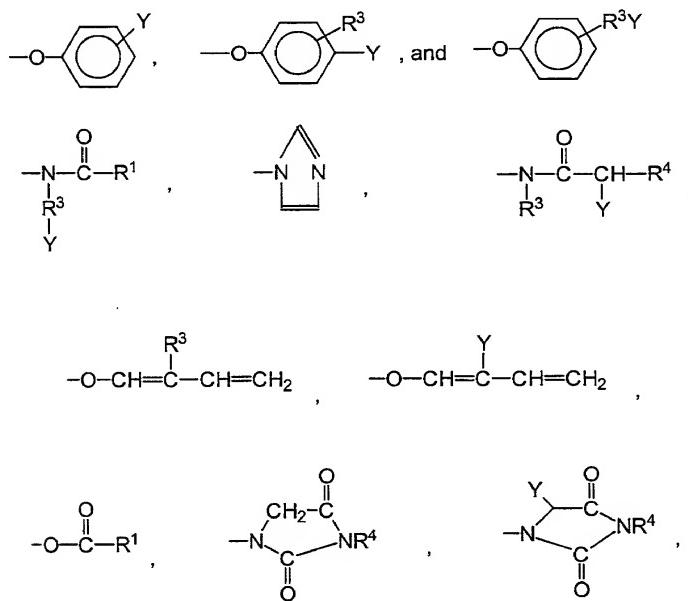
Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the detergent compositions.

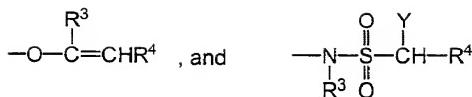
Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving Groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:





and mixtures thereof, wherein R¹ is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R³ is an alkyl chain containing from 1 to 8 carbon atoms, R⁴ is H or R³, and Y is H or a solubilizing group. Any of R¹, R³ and R⁴ may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

The preferred solubilizing groups are -SO₃⁻M⁺, -CO₂⁻M⁺, -SO₄⁻M⁺, -N^{+(R³)₄X⁻ and O<-N(R³)₃ and most preferably -SO₃⁻M⁺ and -CO₂⁻M⁺ wherein R³ is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.}

Alkyl Percarboxylic Acid Bleach Precursors

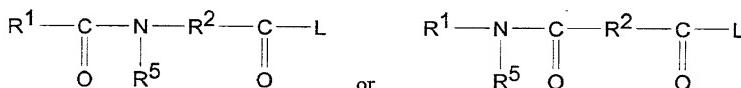
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred. The TAED is preferably not present in the agglomerated particle of the present invention, but preferably present in the detergent composition, comprising the particle.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoxyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

Amide Substituted Alkyl Peroxyacid Precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic Acid Precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic Peroxyacid Precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter.

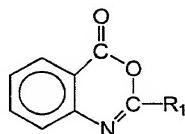
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Benzoxazin Organic Peroxycid Precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

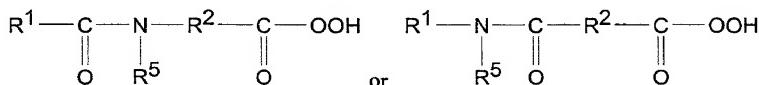


wherein R₁ is H, alkyl, alkaryl, aryl, or arylalkyl.

Preformed Organic Peroxycid

The detergent composition may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R¹ is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxycaproic acid are also suitable herein.

Bleach Catalyst

The composition can contain a transition metal containing bleach catalyst.

One suitable type of bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

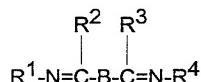
Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2\text{-}(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2\text{-}(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4\text{-}(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2\text{-}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2\text{-}(\text{ClO}_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S.

Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH₃)₃-(PF₆).

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein R¹, R², R³, and R⁴ can each be selected from H, substituted alkyl and aryl groups such that each R¹-N=C-R² and R³-C=N-R⁴ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S, CR⁵R⁶, NR⁷ and C=O, wherein R⁵, R⁶, and R⁷ can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe,-bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include Co(2,2'-bispyridylamine)Cl₂, Di(isothiocyanato)bispyridylamine-cobalt (II), trisdiipyridylamine-cobalt(II) perchlorate, Co(2,2-bispyridylamine)₂O₂ClO₄, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4^+$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2]^- (\text{ClO}_4)_3$.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

The bleach catalyst is typically used in a catalytically effective amount in the compositions and processes herein. By "catalytically effective amount" is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance bleaching and removal of the stain or stains of interest from the target substrate. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some users elect to use very hot water; others use warm or even cold water in laundering operations. Of course, the catalytic performance of the bleach catalyst will be affected by such considerations, and the levels of bleach catalyst used in fully-formulated detergent and bleach compositions can be appropriately adjusted. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 1 ppm to about 200 ppm of the catalyst species in the wash liquor. To illustrate this point further, on the order of 3 micromolar manganese catalyst is effective at 40°C, pH 10 under European conditions using perborate and a bleach precursor. An increase in

concentration of 3-5 fold may be required under U.S. conditions to achieve the same results.

Water-Soluble Builder Compound

The compositions in accord with the present invention preferably contain a water-soluble builder compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 60% by weight, most preferably from 15% to 40% by weight of the composition.

The detergent compositions of the invention preferably comprise phosphate-containing builder material. Preferably present at a level of from 0.5% to 60%, more preferably from 5% to 50%, more preferably from 8% to 40.

The phosphate-containing builder material preferably comprises tetrasodium pyrophosphate or even more preferably anhydrous sodium tripolyphosphate.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and

fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates.

Polycarboxylates or their acids containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447. The most preferred polycarboxylic acid containing three carboxy groups is citric acid, preferably present at a level of from 0.1% to 15%, more preferably from 0.5% to 8% by weight of the composition.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate,

sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

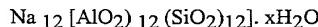
Partially Soluble or Insoluble Builder Compound

The compositions in accord with the present invention may contain a partially soluble or insoluble builder compound, typically present in detergent compositions at a level of from 0.5% to 60% by weight, preferably from 5% to 50% by weight, most preferably from 8% to 40% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula:



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276\text{H}_2\text{O}$.

Another preferred aluminosilicate zeolite is zeolite MAP builder.

The zeolite MAP can be present at a level of from 1% to 80%, more preferably from 15% to 40% by weight of the compositions.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

In a preferred aspect the zeolite MAP detergent builder has a particle size, expressed as a d_{50} value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres.

The d_{50} value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer. Other methods of establishing d_{50} values are disclosed in EP 384070A.

Heavy metal ion sequestrant

The compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 10%, preferably from 0.1% to 5%, more preferably from 0.25% to 7.5% and most preferably from 0.3% to 2% by weight of the compositions or component

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate, 1,1 hydroxyethane diphosphonic acid and 1,1 hydroxyethane dimethylene phosphonic acid.

Other suitable heavy metal ion sequestant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetraacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glycetyl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are also suitable.

Especially preferred are diethylenetriamine pentacetic acid, ethylenediamine-N,N'-disuccinic acid (EDDS) and 1,1 hydroxyethane diphosphonic acid or the alkali

metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Enzyme

Another preferred ingredient useful in the compositions herein is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl, Duramyl and BAN by Novo Industries A/S. Highly preferred amylase enzymes maybe those described in PCT/US 9703635, and in WO95/26397 and WO96/23873.

Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Organic Polymeric Compound

Organic polymeric compounds are preferred additional components of the compositions herein and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein, including quaternised ethoxylated (poly) amine clay-soil removal/ anti-redeposition agent in accord with the invention.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.01% to 30%, preferably from 0.1% to 15%, most preferably from 0.5% to 10% by weight of the compositions.

TECHNICAL FIELD

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 1000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

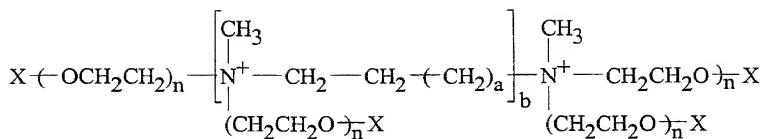
Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Highly preferred polymeric components herein are cotton and non-cotton soil release polymer according to U.S. Patent 4,968,451, Scheibel et al., and U.S. Patent 5,415,807, Gosselink et al., and in particular according to US application no.60/051517.

Another organic compound, which is a preferred clay dispersant/ anti-redeposition agent, for use herein, can be the ethoxylated cationic monoamines and diamines of the formula:



wherein X is a nonionic group selected from the group consisting of H, C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic monoamines (b=0), n is at least 16, with a typical range of from 20 to 35; for cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

Other dispersants/ anti-redeposition agents for use herein are described in EP-B-011965 and US 4,659,802 and US 4,664,848.

Suds Suppressing System

The detergent compositions of the invention, when formulated for use in machine washing compositions, may comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.02% to 10%, most preferably from 0.05% to 3% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component.

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Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkylamine chlorotriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises:

- (a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination
 - (i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

- (ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

- (b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;
- (c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Other highly preferred suds suppressing systems comprise polydimethylsiloxane or mixtures of silicone, such as polydimethylsiloxane, aluminosilicate and polycarboxylic polymers, such as copolymers of laic and acrylic acid.

Polymeric Dye Transfer Inhibiting Agents

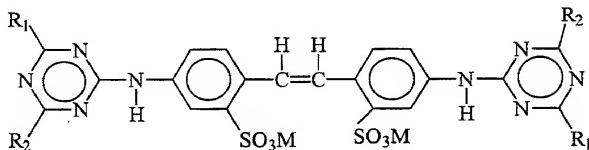
The compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these polymers can be cross-linked polymers.

Optical Brightener

The compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-

Geigy Corporation. Tinopal-CBS-X and Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal SBM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species are commercially marketed under the tradename Tinopal-DMS-X and Tinopal AMS-GX by Ciba Geigy Corporation.

Polymeric Soil Release Agent

Polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such

as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully-anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic

derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C₁-C₄ alkyl celluloses and C₄ hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violand et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violand et al.;

Other Optional Ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, spray-on and encapsulates, colours and filler salts, with sodium sulfate being a preferred filler salt.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C ₁₁ -C ₁₃ alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
CxyAS	:	Sodium C _{1x} - C _{1y} alkyl sulfate
C46SAS	:	Sodium C ₁₄ - C ₁₆ secondary (2,3) alkyl sulfate
CxyEzS	:	Sodium C _{1x} -C _{1y} alkyl sulfate condensed with z moles of ethylene oxide
CxyEz	:	C _{1x} -C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
QAS	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄
QAS 1	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₈ - C ₁₁
SADS	:	Sodium C ₁₄ -C ₂₂ alkyl disulfate of formula 2-(R).C ₄ H ₇ .-1,4-(SO ₄) ₂ where R = C ₁₀ -C ₁₈
MBAS	:	C ₁₂ - C ₁₈ midbranched alkyl sulphate surfactant with an average branching of 1.5 methyl or ethyl branching groups
MES	:	x-sulpho methylester of C ₁₈ fatty acid
APA	:	C ₈ - C ₁₀ amido propyl dimethyl amine
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
STS	:	Sodium toluene sulphonate
CFAA	:	C ₁₂ -C ₁₄ (coco) alkyl N-methyl glucamide
TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
TPKFA	:	C ₁₆ -C ₁₈ topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
TSPP	:	Tetrasodium pyrophosphate

Zeolite A	:	Hydrated sodium aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12}\cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
NaSKS-6	:	Crystalline layered silicate of formula $\delta\text{-Na}_2\text{Si}_2\text{O}_5$
Citric acid	:	Anhydrous citric acid
Borate	:	Sodium borate
Carbonate	:	Anhydrous sodium carbonate with a particle size between 200 μm and 900 μm
Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400 μm and 1200 μm
Silicate	:	Amorphous sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O} = 2.0:1$)
Sulfate	:	Anhydrous sodium sulfate
Mg sulfate	:	Anhydrous magnesium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 μm and 850 μm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
MA/AA (1)	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
CMC	:	Sodium carboxymethyl cellulose
Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
<u>Enzymes:</u>		
Protease	:	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase

Protease I	:	Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
Alcalase	:	Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amyloytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
Amylase II	:	Amyloytic enzyme, as disclosed in PCT/ US9703635
Lipase	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
Endolase	:	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
Percarbonate	:	Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
DOBS	:	Decanoyl oxybenzene sulfonate in the form of the sodium salt
DPDA	:	Diperoxydodecanedioic acid
NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt, optionally comprising a disintegrating agent
NACA-OBS	:	(6-nonamidocaproyl) oxybenzene sulfonate, optionally comprising a disintegrating agent

LOBS	:	Dodecanoxybenzene sulfonate in the form of the sodium salt
DOBS	:	Decanoxybenzene sulfonate in the form of the sodium salt
DOBA	:	Decanoyl oxybenzoic acid
TAED	:	Tetraacetyl ethylenediamine
DTPA	:	Diethylene triamine pentaacetic acid
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
EDDS	:	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2:2'-disulfonate
HEDP	:	1,1-hydroxyethane diphosphonic acid
PEGx	:	Polyethylene glycol, with a molecular weight of x (typically 4,000)
PEO	:	Polyethylene oxide, with an average molecular weight of 50,000
TEPAE	:	Tetraethylenepentaamine ethoxylate
PVI	:	Polyvinyl imidosole, with an average molecular weight of 20,000
PVP	:	Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
PVNO	:	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
QEA	:	bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃) -N ⁺ -C ₆ H ₁₂ -N ⁺ -(CH ₃) bis((C ₂ H ₅ O)-(C ₂ H ₄ O)) _n , wherein n = from 20 to 30

Clay 1	:	Compressed montmorillonite clay, 90% having a particle size of from 400 microns to 100 microns, compressed with a pressure of 20 MPa
Clay 2	:	Compressed bentonite clay, 90% having a particle size of from 400 microns to 100 microns, compressed with a pressure of 20MPa
Clay 3	:	Any clay according to example 1
SRP 1	:	Anionically end capped poly esters
SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
Cellulose	:	cellulose such as Solka-floc or Arbocel or microcrystalline cellulose such as Lattice, form FMC.
PEI	:	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
Opacifier	:	Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
Wax	:	Paraffin wax
Photo-bleach	:	agent comprising zinc or alumino phthalocyanine and polyvinylpyrrolidinone of average molecular weight of 30,000 to 50,000, at a weight ratio of 1:80 to 1:120, encapsulated with starch and with a sugar derivative

Example 1

A compressed clay component was prepared by placing 20 gram of a clay, for example a bentonite or montmorillonite clay, whereof 90% of the particles had a particle

size of below 110 microns, in a die having a diameter of 5.4 cm and compressing the clay into a tablet of about 10 cm thick, by applying a force of 45 kN, using a Lloyd 50K tablet press. The obtained tablet was broken in parts and the parts were added to a Combimax 700 food processor, to thus grind the parts to form the particulate compressed clay component. These particles were sieved to obtain the fraction whereof 95% by weight had a particle size from 500 microns to 1000 microns.

The same process was repeated but then by applying a force of 25kN.

The same process was repeated, both when using a force of 25kN and 45kN, but then compressing an agglomerated bentonite or montmorillonite clay also comprising 10% by weight of the agglomerate of a wax and 5% by weight of the agglomerate of a humectant.

Example 2

Detergent tablets:

	Ex A	Ex B	Ex C	Ex D	Ex E	Ex F
	%	%	%	%	%	%
Clay 3	8.0	10.0	14.5	11.0	15.0	4.0
Flocculant Agglomerate (PEO, zeolite, MA/AA, water)	2.0	1.5	5.8	3.0	-	-
Anionic agglomerates	38	24	38	24	38	24
Cationic agglomerates	5.0	5.0	5.0	5.0	5.0	5.0
Sodium percarbonate	8	8	8	8	8	8
Bleach activator agglomerates	2.31	2.31	2.31	2.31	2.31	2.31
Sodium carbonate	2.67	45.33	17.00	31.00	10.86	37.14
EDDS/Sulphate particle	0.19	0.19	0.19	0.19	0.19	0.19
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.34	0.34	0.34	0.34	0.34	0.34
Fluorescer	0.15	0.15	0.15	0.15	0.15	0.15
Zinc Phthalocyanine sulphonate encapsulate	0.027	0.027	0.027	0.027	0.027	0.027

Soap powder	1.40	1.40	1.40	1.40	1.40	1.40
Suds suppressor	2.6	2.6	2.6	2.6	2.6	2.6
Cellulose	3.0	2.0	1.5	-	-	3.0
Citric acid	4.0	4.0	4.0	4.0	4.0	4.0
Protease	0.45	0.45	0.45	0.45	0.45	0.45
Sodium acetate	0.3	0.5	2.0	-	3.0	-
Cellulase	1.0	0.20	0.30	0.50	0.50	1.20
Amylase	0.20	0.20	0.20	0.20	0.20	0.20
<i>Binder</i>						
Cationic Polymer	0.75	0.75	0.75	0.75	0.75	0.75
PEG 4000	1.25	1.25	1.25	1.25	1.25	1.25

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate.

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate.

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate.

Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active,

Suds suppressor comprises of 11.5% silicone oil; 59% of zeolite and 29.5% of water.

Example 3

Detergent composition in granular form according to the invention:

	G	H	I	J	K	L
Agglomerate						
LAS	7.0	5.0	10.0	14.0	2.0	-
C245AS	3.0	2.0	2.0	2.0	2.5	2.5
Clay 3	10.0	5.0	-	-	-	-
C45AE3S	1.0	1.0	1.0	-	-	0.5
C28AS	2.0	1.0	2.0	1.0	0.5	3.5
Silicate	0.2	-	1.0	-	0.3	0.8
Sodium carbonate	6.0	3.0	8.0	-	3.0	3.0
MBAS	-	2.0	-	-	5.0	8.0
SKS-6	0.7	4.0	-	0.5	1.0	2.0
HEDP/EDDS	0.1	0.7	0.3	-	-	0.5
Zeolite A	10.0	6.0	6.0	12.0	9.0	10.0
CMC	0.5	-	0.3	0.8	-	0.5
Agglomerate						
TAED	5.0	3.0	-	2.0	4.0	3.0
CMC or MA/AA	1.0	0.5	-	0.5	1.0	1.0
Clay 3	-		-	-	-	2.0
Agglomerate						
Zeolite A	2.0	1.0	-	1.0	-	2.0
Suds suppressor	0.5	0.5	0.3	0.2	0.1	0.2
MA/AA	0.5	-	-	0.2	-	0.2
Agglomerate						
QAS	1.0	0.5	1.0	-	1.0	-

Zeolite	2.0	1.0	-	-	2.0	-
Carbonate	0.5	1.0	-	-	-	-
MA/AA	-	0.1	-	-	-	-
PEO	5.0	-		1.5	3.0	2.0
Clay 3	-	-	-	10.0	4.0	5.0
Dry add						
QEA	1.0	0.5	-	-	1.0	-
Clay 3	5.0	2.0	12.0	10.0	8.0	2.0
HEDP/DTPA/EDDS	0.3	0.5	-	0.5	0.5	0.5
MA/AA	1.0	2.0	3.0	-	2.0	2.0
Mg sulphate	0.1	0.2	-	-	-	0.3
Brightener	0.1	-	0.2	0.2	-	0.2
Zeolite	1.0	2.0	3.0	4.0	5.0	2.0
SKS-6/silicate	10.0	6.0	5.0	10.0	10.0	12.0
Enzymes	0.5	0.8	0.3	1.2	1.2	1.0
CMC	0.2	-	0.3	-	0.5	0.5
Soap	0.5	-	-	0.5	1.0	-
NACA OBS	-	3.0	-	-	-	3.0
Photobleach	0.1	0.1	0.5	-	0.2	-
Speckles	0.5	0.2	0.7	-	0.3	-
Carbonate	6.0	5.0	2.0	-	8.0	7.0
Sodium chloride	0.2	-	0.5	-	0.5	-
Sodium sulphate	2.0	3.0	-	8.0	-	3.0
Percarbonate	18.0	10.0	-	22.0	20.0	10.0
Citric acid	1.0	0.5	2.0	3.0	2.0	-
Spray on						
AE5	-	0.5	-	-	2.0	-
Perfume	0.2	0.1	0.5	0.2	0.2	0.2
Brightener	0.1	0.2	0.1	0.1	0.1	0.1
Photobleach	-	-	-	-	-	0.01

Example 4

Detergent composition according to the invention, in granular form:

	M	N	O	P	Q	R
Spray dried powder						
Base: LAS	7.0	6.0	3.0	-	4.0	-
MBAS	-	-	-	5.0	-	-
SADS	-	-	-	-	3.0	-
Tallow alkyl sulphate	1.0	-	1.0	1.0	-	1.0
C245AS	-	-	0.5	-	-	1.0
Sodium sulphate	3.0	5.0	3.0	2.0	-	3.0
C24AE35	-	0.5	-	0.5	-	0.7
Clay 1 or 2	10.0	-	-	-	-	-
PEO	0.5	1.5	3.0	4.0	5.0	2.0
Sodium carbonate	3.0	6.0	1.0	3.0	5.0	3.0
Sodium sulphate	-	1.0	2.0	2.0	-	5.0
Zeolite A	16.0	10.0	5.0	10.0	6.0	-
MA/AA	1.0	-	1.0	0.5	1.0	-
Mg sulphate	0.1	0.1	-	0.1	-	0.1
Brightener	0.2	0.1	-	-	0.3	0.5
Chelant	0.5	0.5	-	0.3	0.2	0.4
Water	0.2	0.1	0.1	0.05	0.05	0.3
Agglomerate						
LAS	-	3.0	5.0	2.0	-	5.0
C45AS	-	2.0	3.0	2.0	-	-
Carbonate	-	5.0	7.0	5.0	-	-
Sulphate	-	3.0	-	2.0	-	3.0
Zeolite A	-	4.0	8.0	3.0	-	9.0
Photobleach	-	0.05	0.05		-	-
Dry add						

QEА	1.0	1.0	1.0	-	1.0	-
Sudsuppressor	0.5	0.5	0.5	1.0	0.2	0.3
Percarbonate/perborate	20.0	14.0	-	22.0	18.0	10.0
TAED	4.0	3.0	-	-	2.0	3.5
NACA OBS	-	3.0	-	4.2	2.5	-
Zeolite A	6.0	3.0	5.0	-	7.0	12.0
SKS-6/silicate	8.0	12.0	5.0	9.0	-	8.0
Citric acid/citrate	2.0	1.0	3.0	-	-	2.0
Speckle (carbonate)	0.3	0.5	0.4	-	-	0.5
Sodium carbonate	5.0	-	8.0	10.0	-	6.0
Sodium sulphate	10.0	5.0	-	3.0	-	14.0
Clay 2 or 3	-	15.0	12.0	4.0	6.0	10.0
Soap	0.5	0.5	-	-	0.5	-
Enzymes	1.0	1.5	1.0	1.0	1.0	1.0
SRP	0.1	0.2	0.3	-	0.3	-
HEDP/EDDS/DTPA	0.5	0.5	-	0.2	0.8	0.3
Spray-on						
AE5	-	3.0	1.5	-	-	-
Perfume	0.3	0.3	0.2	0.5	0.2	0.3

Example 5

	S	T	U	V	W	X
Blown powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AE35	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
SADS	0.5	-	-	-	-	-
Zeolite A	10.0	18.0	14.0	12.0	10.0	14.0
MA/AA	-	0.5	-	-	-	2.0
MA/AA(1)	7.0	-	-	-	-	-
Clay 1 or 3	-	-	6.0	10.0	-	-
Sulfate	5.06.3	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
Photobleach 2	-	0.05	0.005	-	0.3	0.5
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray-on						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0
PEO	-	3.0	3.0	2.0	-	1.0

Clay 3		3.0	-	7.0	-	5.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (water etc)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS (I)	-	-	-	-	1.0	-
Clay 2 or 3	3.0	-	6.0	-	11.0	6.0
Citric acid/ malic acid	-	-	5.0	3.0	2.0	5.0
PB4	-	-	-	-	12.0	1.0
PB1	-	4.0	3.0	-	-	-
Percarbonate	4.0	-	-	2.0	-	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6
Methyl cellulose	0.2	-	-	-	-	-
SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Cumene sulfonic acid	-	1.0	-	-	-	2.0
Photobleach	0.01	-	-	0.1	0.1	-
Lipase	0.2	-	0.2	-	0.2	0.4
Cellulase	0.2	0.2	0.2	0.3	0.2	0.2
Amylase	0.2	-	0.1	-	0.2	-
Protease	0.5	0.5	0.5	0.3	0.5	0.5
PVPI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP1	0.2	0.5	0.3	-	0.2	-
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-

Silica	0.2	0.2	0.2	-	0.2	-
Misc/minors to 100%						

Example 6

The following nil bleach-containing detergent formulations of particular use in the washing of coloured clothing, according to the present invention were prepared:

	Y	Z	AA
Blown Powder			
Zeolite A	15.0	15.0	-
Sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
PEO	2.0	1.0	1.5
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Photobleach 2	-	0.005	-
Spray On			
EFAA	-	2.0	-
Perfume	0.3	0.3	0.5
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0

NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4
Clay 3	11.0	7.0	10.0
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Sulfate	0.0	9.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	700	700	700

Example 7

The following is a composition in the form of a tablet or granular formulation in accord with the invention.

	BB	CC	DD	EE	FF	GG	HH	II	JJ	KK	LL
Sodium C ₁₁ -C ₁₃ alkylbenzenesulfonate	12.0	16.0	23.0	19.0	18.0	20.0	16.0	8.5	5	20.0	6.0
Sodium C ₁₄ -C ₁₅ alcohol sulfate		4.5	-		-	-	4.0		-	-	-
C ₁₄ -C ₁₅ alcohol ethoxylate (0.5) sulfate			-	-	-	-	-	-	-	-	-
C ₁₄ -C ₁₅ alcohol ethoxylate (3) sulfate	-	-	2.0	-	1.0	1.0	1.0	-	-	-	-
Sodium C ₁₄ -C ₁₅ alcohol ethoxylate (or mixtures of different ethoxylation degree)	2.0	2.0	-	1.3	-	-	5.0	5.5	4.0	-	-

C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt			-	-	1.0	0.5	2.0	-	-	-	-
Tallow fatty acid			-	-	-	-	1.0	-	-	-	-
Tallow alcohol ethoxylate (50)	-	-	-	-	-	-	-	-	-	-	-
Sodium tripolyphosphate / Zeolite	23.0	25.0	14.0	22.0	20.0	10.0	20.0	30.0	20.0	25.0	25.0
Sodium carbonate	25.0	22.0	35.0	20.0	28.0	41.0	30.0	30.0	25.0	45.0	24.0
Sodium Polyacrylate (45%)	0.5	0.5	0.5	0.5	-	-	-	-	-	-	-
Sodium polyacrylate/maleate polymer	-	-	1.0	1.0	1.0	2.0	0.5	0.5	1.0	-	-
Sodium silicate (1:6 ratio NaO/SiO ₂)(46%)	3.0	6.0	9.0	8.0	9.0	6.0	8.0	5.0	6.0	8.0	5.0

Sodium sulfate	-	-	-	-	-	2.0	3.0	-	-	-	8.0
Sodium perborate/percarbonate	5.0	5.0	10.0	-	3.0	1.0	-	20.0	14.0	-	-
Poly(ethylene glycol), MW ~4000 (50%)	1.5	1.5	1.0	1.0	-	-	0.5	-	-	-	0.5
Sodium carboxy methyl cellulose	1.0	1.0	1.0	-	0.5	0.5	0.5	0.5	0.5	-	0.5
Citric acid	-	-	-	-	-	-	-	-	-	-	-
NOBS/DOBS	-	1.0	-	-	1.0	0.7	-	-	-	-	-
TAED / PAP	1.5	1.0	2.5	-	3.0	0.7	-	4.5	5.0	-	-
Chelant	0.5	0.5	0.5	-	1.0	-	-	0.5	0.5	-	-
SRP	1.5	1.5	1.0	1.0	-	1.0	-	1.0	1.0	-	-
Clay 3	5.0	6.0	12.0	7.0	10.0	4.0	3.0	7.0	10.0	6.0	8.0
Flocculating agent PEO	0.2	0.2	3.0	2.0	0.1	1.0	0.5	2.0	0.5	1.0	0.5
Humectant	-	-	-	-	0.5	0.5	-	-	0.5	-	-
wax	0.5	-	-	-	-	0.5	-	-	0.5	-	-
Cellulose	0.5	2.0	-	-	3.0	2.0	-	-	1.5	-	1.0
Sodium acetate	2.0	1.0	3.0	-	-	-	-	1.0	0.5	4.0	1.0
Moisture	7.5	7.5	6.0	7.0	5.0	3.0	5.0	5.0	5.0	8.0	10.0
Magnesium sulphate	-	-	-	-	-	0.5	1.5	-	-	-	-

Soap/ suds suppressor	-	-	0.5	0.5	0.8	0.6	1.0	1.0	0.8	0.5/ 0.0	1.0/ 0.0
Enzymes, including amylase, cellulase, protease and lipase	-	-	-	-	2.0	1.5	2.0	0.5	1.0	1.0	1.0
Speckle	2.5	1.1	0.5	1.4	-	-	2.2	1.0	1.6	1.0	
minors, e.g. perfume, PVP, PVPVI/PVN O, brightener, photo-bleach,	2.0	1.0	1.0	1.0	2.5	1.5	1.0	1.0	0.5	0.5	0.5

Claims

1. A cleaning composition or component thereof comprising a compressed clay component.
2. A tablet comprising an active ingredient and a compressed clay component.
3. A tablet, composition or component according to claim 1 or 2 obtainable by compressing a clay material to form a compressed clay component and subsequently incorporation of the compressed clay component in the tablet, cleaning composition or component.
4. A tablet, composition or component according to any preceding claim, whereby the clay component is obtained by compression of a clay material with a pressure of at least 10 MPa.
5. A tablet, composition or component according to any preceding claim whereby the compressed clay component is in the form of particles whereof at least 90% by weight has a particle size of from 200 microns to 1500 microns.
6. A tablet, composition or component according to any preceding claim whereby the clay component comprises a binder material.
7. A tablet, composition or component according to any of claims 1 to 5 whereby the clay component is free of any added binder materials other than water.
8. A tablet, composition or component according to any preceding claim whereby the clay comprises a smectite clay.

9. A tablet, composition or component according to any preceding claim comprising one or more additional disintegrating agents, preferably a water soluble salt such as sodium acetate, and/ or a microcrystalline cellulose.
10. A tablet or composition according to any preceding claim being a solid laundry or dishwashing tablet or composition and comprising from 0.5% to 30% by weight of the composition or tablet of the compressed clay component.
11. A tablet according to any of claims 1 to 9 being a pharmaceutical tablet.
12. A compressed clay granule comprising a clay material and an effervescence system which comprises an acid source and a carbonate source, and/ or a disintegrating agent, preferably selected from water-swellable materials, microcrystalline cellulose and/ or water soluble salts.
13. A pharmaceutical composition, plant nutrient composition or plant fertilizer composition comprising a compressed clay component.
14. Use of a compacted clay component in a granular composition or tablet, in particular a cleaning composition or tablet plant nutrient composition or tablet, plant fertilizer compositions or tablet, or pharmaceutical compositions or tablet, to improve the dissolution or disintegration of the composition or tablet.
15. Use of a cleaning composition or tablet according to claim 8 to provide softening of fabrics treated with the composition or tablet.

DECLARATION COMBINED WITH POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"Cleaning Compositions and Tablets"

bearing the above listed Procter & Gamble Company Case number, the specification of which was filed as PCT/US00/10272, designating at least the United States of America, with the United States Receiving Office on 13 April 2000.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37 Code of Federal Regulations §1.56.

I hereby claim foreign priority benefits under Title 35 United States Code §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application for patent or Inventor's certificate having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S) TO WHICH WE CLAIM PRIORITY:

9909898.0 GB 30 April 1999

I hereby claim the benefit under Title 35 United States Code §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37 Code of Federal Regulations §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

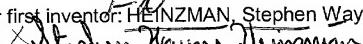
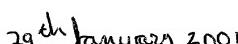
Appln. Serial No.	Filing Date	Status - patented, pending, abandoned
Appln. Serial No.	Filing Date	Status - patented, pending, abandoned

I hereby appoint the following as my attorney(s) or agent(s) with full power of substitution to prosecute this application and transact all business in the Patent and Trademark office connected therewith:

Name	Registration No.	Associate Power of Attorney Attached
Jacobus C. Rasser	37,043	[<input type="checkbox"/>] Yes [<input type="checkbox"/>] No
Donald E. Hasse	29,387	
T. David Reed	32,931	
Eileen L. Huggett	34,352	
Timothy B. Guffey	41,048	
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		Zip Code

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor: HEINZMAN, Stephen Wayne

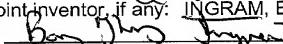
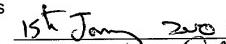
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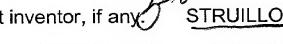
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Full name of third joint inventor, if any: STRUILLOU, Arnaud Pierre

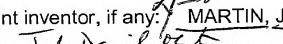
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DECLARATION COMBINED WITH POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"Cleaning Compositions and Tablets"

bearing the above listed Procter & Gamble Company Case number, the specification of which was filed as PCT/US00/10272, designating at least the United States of America, with the United States Receiving Office on 13 April 2000.

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PRIOR FOREIGN APPLICATION(S) TO WHICH WE CLAIM PRIORITY:

9909898.0 GB 30 April 1999

I hereby claim the benefit under Title 35 United States Code §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37 Code of Federal Regulations §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Appln. Serial No.	Filing Date	Status - patented, pending, abandoned
Appln. Serial No.	Filing Date	Status - patented, pending, abandoned

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Inventor's signature Malcolm Curtis Date 5th DECEMBER 2000
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hereby appoint the following as my attorney(s) or agent(s) with full power of substitution to prosecute this application and transact all business in the Patent and Trademark office connected therewith:

Name	Registration No.	Associate Power of Attorney Attached
Jacobus C. Rasser	37,043	[] Yes [] No
Donald E. Hasse	29,387	
T. David Reed	32,931	
Eileen L. Huggett	34,352	
Timothy B. Guffey	41,048	
Emelyn L. Hiland	41,501	

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor: HEINZMAN, Stephen Wayne
Inventor's signature _____ Date _____

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Inventor's signature Barry Thomas Date 15th January 2001

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